Atomic Layer Deposition: Process Models and Metrologies

Atomic layer deposition is increasingly used to deposit thin (nanometer-scale) conformal layers that are required for many microelectronics applications, including high κ gate dielectric layers, diffusion barrier layers, copper seed layers, and DRAM dielectric layers. However, significant developmental issues remain for many of these applications. NIST goal is to provide validated, predictive atomic layer deposition (ALD) models and in situ diagnostics for ALD processes.

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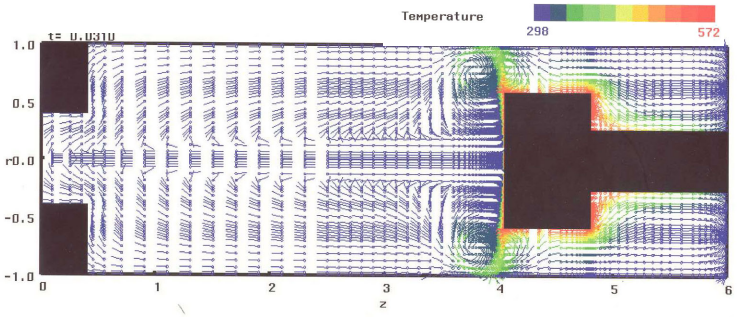
Technology computer-aided design (TCAD) is a potential solution to many atomic layer deposition (ALD) developmental issues. TCAD uses validated ALD process models to predict equipment influences on film properties. TCAD has been identified in the 2003 International Technology Roadmap for Semiconductors as "one of the few enabling methodologies that can reduce development cycle times and costs." [Modeling and Simulation, p. 1] However, TCAD requires physical and chemical data including: rate constants, cross sections, surface chemistry, reaction mechanisms, and reduced models for complex chemistry. Beyond data, experimental validation has been identified as a "key difficult challenge across all modeling areas." [Modeling and Simulation, p. 1] For experimental validation, the Roadmap notes that "major effort required for better model validation is without doubt sensor development." [Modeling and Simulation, p. 15] This project will address some ALD developmental issues by developing validated, predictive process models and associated metrologies for ALD processes.

This research has two primary thrusts: (1) development of validated, predictive ALD models and (2) development of *in situ* diagnostics for ALD processes. ALD process models are being improved by incorporating NIST-developed chemical reaction mechanisms into commercially-available computational fluid dynamics (CFD) codes and then by validating the process model under a range of conditions using NIST-collected experimental data. Initially, theoretical investigations have focused on ALD of Al_2O_3 (aluminum oxide) from TMA (trimethylaluminum) and water as a test case for the more complex analysis of HfO_2 (hafnium oxide) ALD. Molecular structures and energies for precursors, adsorbates, intermediates, and transition states have been calculated using *ab initio* and density functional theory quantum calculations for ALD of Al_2O_3 from TMA and water. Prototypical small cluster ($Al_xO_yH_z$) species have been utilized to represent the surface layer. Rate expressions based on calculated structures and energies have been derived using transition state theory. A detailed chemical kinetic model for ALD of Al_2O_3 from TMA and water has been constructed based on these rate expressions. This model is being refined by further simulations of reactor models, comparisons with experimental observables, and, where necessary, by additional quantum calculations.

High level *ab initio* calculations using coupled-cluster theory up to CCSD(T)/aug-cc-pVnZ (n=2-4) have been completed for small species to benchmark heats of formation and bond dissociation energies for AlHnX species (n = 0-2, X = H, F, Cl, OH, NH_2, CH_3). Additional calculations will be done to provide higher level corrections (e.g., core-valence, relativistic, etc). A two-dimensional CFD model has been developed for our experimental ALD reactors. Numerical solutions have been obtained for flow by a heated substrate with and without full chemistry for ALD of Al_2O_3 from TMA and water. Simulations of OH and CH_3 surface coverages agree well with experimental measurements reported in the literature. Work is ongoing in adjusting rate expressions to reproduce experimental growth rates. The energetics for several prototypical species/reactions for HfO_2 ALD have been computed using quantum calculations. A relatively simple chemical mechanism for HfO_2 ALD has been developed. This HfO_2 chemical mechanism has been incorporated into the two-dimensional flow model and the benchmarking of results has begun.

Numerical simulation of the flow field in the ALD reactor operating at a chamber pressure of 133 Pa (1 Torr), an inlet gas flow rate of 200 standard cubic centimeters per minute and a wafer surface temperature of 572 K.



To generate model validation data as well as to develop process diagnostics, research-grade, optically-accessible ALD reactors have been designed and constructed with full optical access for surface and gas-phase Raman and infrared absorption spectroscopic measurements. An associated pulsed gas delivery system was also designed and constructed. ALD HfO_2 films were deposited from tetrakis (dimethylamino) hafnium or tetrakis (ethylmethylamino) hafnium and water under a range of deposition conditions.

Ex situ characterization of these films has been performed, including vacuum ultraviolet spectroscopic ellipsometry and X-ray diffractometry. *In situ* gas phase and surface Raman spectroscopy have been performed under deposition conditions. An *in situ* gas phase and surface infrared absorption spectroscopic optical system is being assembled.

Successful development of validated ALD process models and *in situ* process diagnostics will result in improved efficiency of reactor design and deposition condition selection and optimization, resulting in savings of time and money and increased utilization of ALD.

Future Directions:

During the upcoming year, *in situ* gas phase and surface optical measurements will continue in an effort to provide model validation data and to develop suitable *in situ* diagnostics for ALD processes. Concurrently, we will search for correlations between specific film deposition steps uncovered by the more sophisticated optical methods with signals from conventional process monitors, such quartz crystal microbalances and mass spectrometers. In addition, we will attempt to correlate data measured *in situ* at or near the deposition surface with data measured in the exhaust stream in an effort to qualify the results of sensors designed for use on reactor exhaust lines.